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Multimodular Engineering of Linear Supramolecular Miniatures on Ag(111) Surfaces Controlled by Complementary Triple *H*-Bonds**

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I. SYNTHESIS

All final compounds were fully characterized (m.p., IR, ^{1}H and ^{13}C NMR, ES-MS). NMR spectra were obtained on a Jeol JNM-EX400 (400 MHz ^{1}H-NMR) and on a Varian Gemini 200 spectrometer (200 MHz ^{1}H-NMR and 50 MHz ^{13}C-NMR). Chemical shifts are reported in ppm using the solvent residual signal as an internal reference ($CDCl_3$: d_H = 7.26 ppm, d_C = 77.16 ppm; Me_2SO-d_6: δ_H = 2.50 ppm, δ_C = 39.52 ppm). The resonance multiplicity is described as *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *dd* (doublet of doublets), *m* (multiplet), *br* (broad signal). IR spectra (KBr) were recorded on a Perkin Elmer 2000 spectometer by Mr. Paolo de Baseggio. Mass spectrometry measurements: Electrospray Ionization (ESI) performed on a Perkin-Elmer API1 at 5600 eV and Electron Impact (EI) performed on a Ion trap GCQ Finnigan Thermoquest at 70 eV

were recorded at Università degli Studi di Trieste by Dr. Fabio Hollan. Melting Point (m.p.) was measured on a *Büchi* SMP-20. THF and NEt_3 were distilled from Na/benzophenone and CaH_2 respectively. All molecules were subject to thermal analysis; in particular thermogravimetry (TG) and differential scanning calorimetry (DSC) were done to study the thermal stability (see below). Decomposition temperatures higher than the temperature used for the deposition on surfaces were found.

4,4'-[(phen-1,4-diyl)diethynyl]bis(2,6-diacetylaminopyridine) (1)

Dry Et_3N (10 mL) and dry THF (10 mL) were added in a Schlenk tube. The solution was degassed by one "freeze-pump-thaw" cycle. 1,4-Diodobenzene (0.07 g, 0.22 mmol), $[Pd(PPh_3)_4]$ (0.01 g, 0.009 mmol) and CuI (3 mg, 0.018 mmol) were then added and the solution was degassed a second time. Finally, ethynylpyridine derivative **7** (0.120 g, 0.55 mmol) was added, the reaction mixture was degassed one more time and the whole mixture stirred overnight at 85 °C under Ar. After 1 hour of reaction a white precipitate appeared. The solvent was concentrated under vacuum and the crude was purified by several precipitations from $CHCl_3$ by adding MeOH yielding **1** (0.9 g, 83%) as a pale yellow solid. **M.p.** ~260°C the compound

burned not melted; **^{1}H NMR** (400 MHz, DMSO-d_6): δ 10.25 (*s*, 4 H; CH_3CON*H*-Ar); 7.9 (*s*, 4 H; Ar-*H*); 7.7 (*s*, 4 H; benzene-*H*); 2.1 (s, 12 H; C*H*$_3$CONH-Ar). **^{13}C-NMR** (50 MHz, DMSO-d_6): δ 169.53, 150.69, 132.82, 132.13, 122.10, 110.26, 91.63, 89.54, 24.09. **IR** (cm^{-1}): ν 3296.7, 2217.3, 1672.3, 1612.1, 1557.6, 1416.4, 1370.3, 1278.8, 1239.6, 1205.7, 1026.9, 1002.3, 859.8, 629.3, 568.3; **MS** (5600 eV, ESI): Found 531.2, (M^+) $C_{28}H_{24}N_6O_4$ requires: 508.53.

1,1'-hexyl-6,6'-[(phen-1,4-diyl)diethynyl]bisuracil (2)

Dry Et_3N (4 mL) and dry THF (4 mL) were added in a Schlenk tube. The solution was degassed by one "freeze-pump-thaw" cycle. 1,4-Diodobenzene (0.012 g, 0.036 mmol), [$Pd(PPh_3)_4$] (1 mg, 0.001 mmol) and CuI (1 mg, 0.003 mmol) were then added and the solution was degassed a second time. Finally, ethynyluracil derivative **12** (0.02 g, 0.09 mmol) was added, the reaction mixture was degassed one more time and the whole mixture stirred overnight at r.t. under Ar. After 1 hour of reaction a white precipitate appeared. The solvent was concentrated under vacuum and the crude was purified by several precipitations from $CHCl_3$ by adding MeOH yielding **2** (0.013 g, 73%) as a white solid. **M.p.** 275-280 ºC; **^{1}H NMR** (400 MHz, DMSO-d_6): δ 11.52 (*br*, 2 H; CON*H*CO); 7.76 (*s*, 4 H; benzene-H); 6.05 (*s*, 2 H; COC*H*); 3.9 (*t*, 4 H; NCH_2); 1.6 (*m*, 4 H; NCH_2CH_2); 1.3

(*m*, 12 H; $NCH_2CH_2CH_2CH_2CH_2CH_3$); 0.9 (*t*, 6 H; CH_2CH_3); **^{13}C-NMR** (50 MHz, DMSO-d_6): δ 162.11; 150.48; 136.92; 132.37; 121.60; 106.69; 97.60; 82.93; 45.65; 30.85; 28.22; 25.70; 22.00; 23.84; **IR** (cm^{-1}): ν 3445.9, 3019.3, 2928.1, 2857.6, 2214.2, 1720.2, 1674.8, 1582.4, 1509.0, 1466.9, 1418.2, 1392.5, 1364.8, 1325.1, 1276.0, 1169.5, 1122.1, 835.7, 814.1, 756.1, 579.4, 543.3; **MS** (70 eV, EI): Found 514, (M^+) $C_{30}H_{34}N_4O_4$ requires: 514,62.

1-Hexyl-6-[(anthracen-9-yl)ethynyl]uracil (3)

Dry THF (5 mL) and iPr_2NH (5 mL) were added to a Schlenk tube. The solution was degassed by one “freeze-pump-thaw” cycle. Iodouracil derivative **10** (0.160 g, 0.5 mmol), [$Pd(OAc)_2$] (2 mg, 0.01 mmol), CuI (4 mg, 0.015 mmol), PPh_3 (8 mg, 0.025 mmol) were then added and the solution was degassed a second time. Finally, 9-Ethynylanthracene (0.120 g, 0.6 mmol) was added, the reaction mixture was degassed one more time and the whole mixture stirred overnight at 85 °C under Ar. The resulting dark mixture was filtered over celite and washed with toluene (10 mL), CH_2Cl_2 (20 mL) and MeOH (20 mL). Removal of the solvents under vacuum and purification of the crude by CC (cyclohexane/EtOAc 6:4) and reprecipitation with cyclohexane yielded **3** (50 mg, 25%) as an orange solid. **M.p.** 215-220 °C. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.6 (*s*, 1 H,

Ant-H), 8.35 (*d*, 2 H, Ant-H), 8.05 (*d*, 2 H, Ant-H), 7.65 (*t*, 2 H, Ant-H), 7.55 (*t*, 1 H, Ant-H), 6.27 (*s*, 1 H; COC*H*); 4.25 (*t*, 2 H; NCH_2); 1.9 (*m*, 2 H; NCH_2CH_2); 1.5 (*m*, 2 H; $NCH_2CH_2CH_2CH_2CH_2CH_3$); 1.3 (*m*, 4 H; $NCH_2CH_2CH_2CH_2CH_2CH_3$); 0.8 (*t*, 3 H; CH_2CH_3); **^{13}C-NMR** (50 MHz, DMSO-d_6): δ 162.16, 150.58, 139.08, 133.47, 131.02, 129.27, 128.05, 126.19, 125.57, 113.48, 106.93, 98.45, 90.99, 83.96, 47.28, 31.65, 29.26, 28.81, 22.74, 14.11. **IR** (cm^{-1}): ν 3422.9, 3164.0, 3042.6, 2929.2, 2854.3, 2193.1, 1678.1, 1587.6, 1446.8, 1409.0, 1349.5, 1323.1, 1177.9, 1014.6, 887.5, 845.0, 756.4, 736.3, 612.5, 550.3; **MS** (70 eV, EI): Found 396, (M^+) $C_{26}H_{24}N_2O_2$ requires: 396.48.

II. SAMPLE PREPARATION FOR STM IMAGING

The experiments were performed in a standard UHV system, consisting of different chambers for sample preparation and characterization (base pressure of 10^{-10} mbar). As metal substrate, a Ag(111) single crystal was prepared by subsequent cycles of Ar+ sputtering and thermal annealing at 500°C. All molecules were deposited onto flat Ag(111) surfaces (kept at 298 K) by organic beam deposition from a glass crucible that was heated inside a commercial evaporator (Kentax UHV equipment) with a deposition rate controlled by a quartz crystal microbalance. In the case of co-deposition of different modules, the individual molecular components were evaporated consecutively. The samples were analyzed with a commercial LT-STM (Omicron NanoTechnology GmbH) at 77K. The tunneling current and voltages for the different samples are given in the text while the bias voltage is specified with respect to a grounded tip. The free software WSxM (I. Horcas , R. Fernandez, J. M. Gomez-Rodriguez, J. Colchero, J. Gomez-Herrero, A.M. Baro, Rev. Sci. Instrum. 2007, 78, 013705) was used for data processing of the STM images.

III. THERMOGRAVIMETRICAL ANALYSIS OF MODULES 1, 2 AND 3

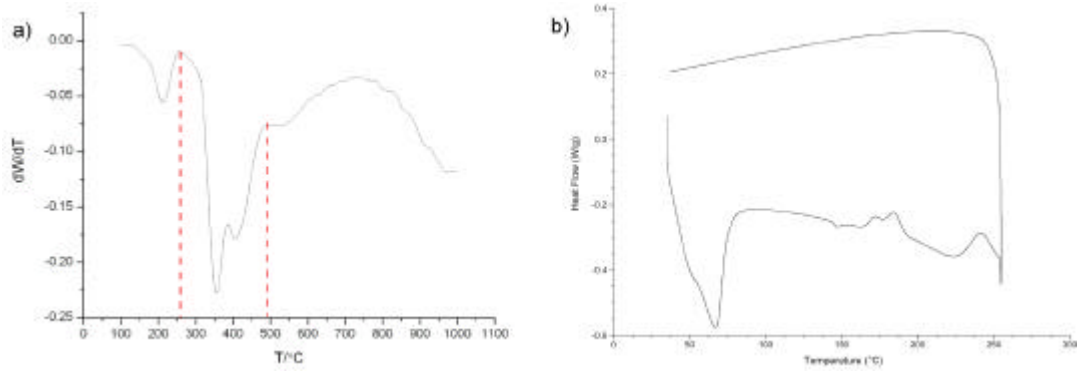

Figure S1: a) dTGA under N_2 of module **1**; b) DSC under N_2 of module **1**.

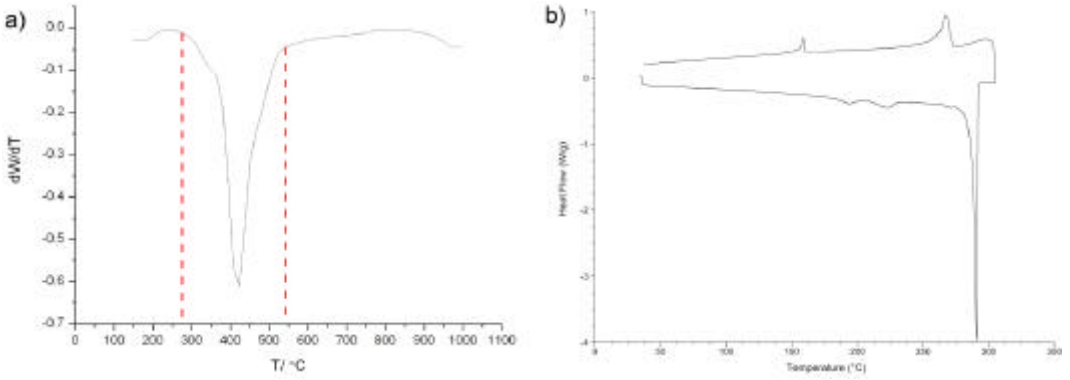

Figure S2: a) dTGA under N_2 of module **2**; b) DSC under N_2 of module **2**.

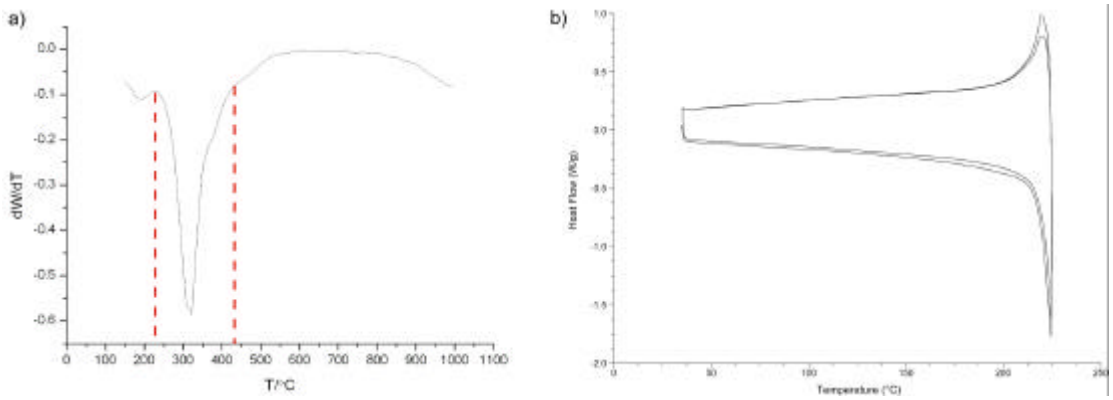

Figure S3: a) dTGA under N_2 of module **3**; b) DSC under N_2 of module **3**.

III. STM

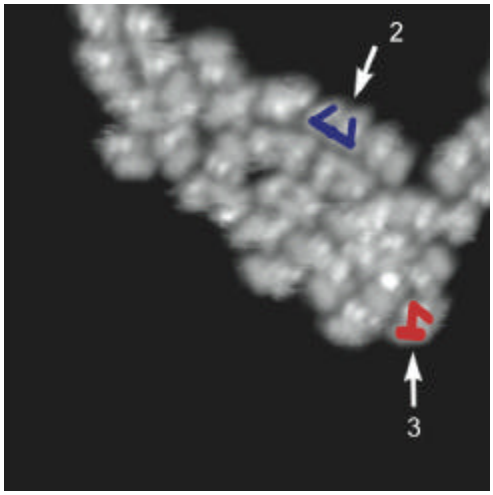

Figure S4: STM image for submonolayer coverage of molecules **2** and **3** (13 nm × 13 nm, 2.4V, 13pA). When mixed-assemblies were observable, they exhibited no regular structures. The white arrows exemplarily indicate one position of **2** and **3**, respectively. The molecules were deposited consecutively while the sample was held at approximately 383 K.

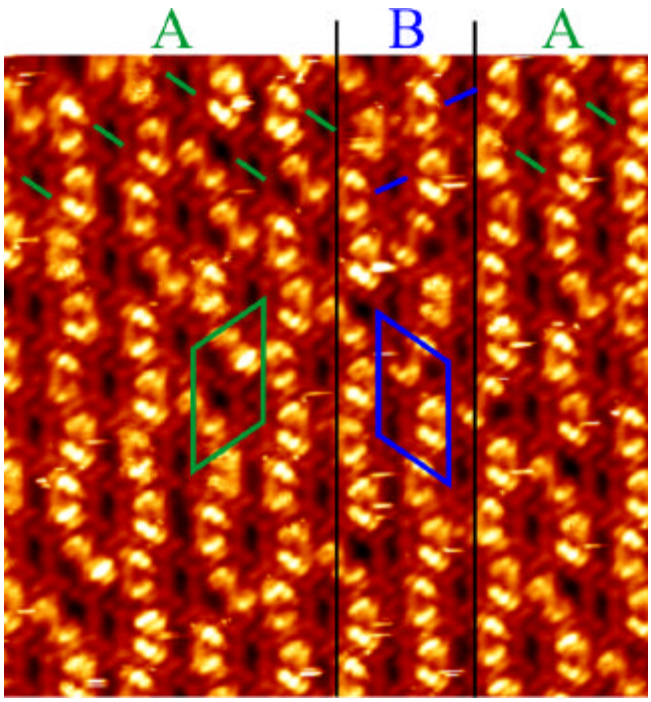

Figure S5: STM image for submonolayer coverage of molecules **1** and **2** (17.5 nm × 17.5 nm, 1.7V, 20pA). Although the STM studies show a well ordered mixed assembly a unique unit cell cannot be derived for the entire structure as the orientation between two adjacent molecules **1** of neighbouring rows (indicated by blue and green lines) flips irregularly. Thus the assembly divides into two regions denoted as A and B. Both regions can be described by identical unit cells with respect to their dimensions. However, the transition to another region implies a mirroring of the unit cell along a straight line perpendicular to the molecular chains. This is highlighted by the unit cells shown in regions A and B. The irregular width of both regions can be observed in larger images (data not shown here).